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As part of an integrated computational materials design effort, quantum mechanical calculations have predicted the roles of impurity and alloying elements in grain boundary cohesion to support design of hydrogen-resistant ultrahigh-strength steels. Predicted thermodynamic quantities have been integrated in systems design of new steels employing W, Re and B for enhanced cohesion. A prototype steel has demonstrated an ultimate tensile strength of 330 ksi with good toughness and ductility, while maintaining desired grain boundary composition.

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ELECTRONIC-LEVEL DESIGN OF STRESS-CORROSION RESISTANT ALLOYS: QUANTUM STEELS

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Abstract: As part of an integrated computational materials design effort, quantum mechanical calculations have predicted the roles of impurity and alloying elements in grain boundary cohesion to support design of hydrogen-resistant ultrahigh-strength steels. Predicted thermodynamic quantities have been integrated in systems design of new steels employing W, Re and B for enhanced cohesion. A prototype steel has demonstrated an ultimate tensile strength of 330 ksi with good toughness and ductility, while maintaining desired grain boundary composition.

RESEARCH SUMMARY

The multi-institutional Steel Research Group (SRG) program centered at Northwestern is directed at the methodology, tools and databases for the computational systems design of materials, using high performance alloy steels as a prototypical case. Our ONR-sponsored interdisciplinary research, integrating materials science and quantum physics, has established the electronic-level principles underlying the role of impurities and alloying elements in intergranular cohesion, and applied them in the design of UHS steels with enhanced resistance to hydrogen stress-corrosion cracking.

Based on the Rice-Wang thermodynamic model of intergranular embrittlement, electronic calculations have been directed at the difference in energy and underlying electronic structure for segregating solutes by comparing their states at grain boundaries and corresponding free surfaces. After preliminary calculations with Embedded Cluster Density Functional (ECDF) methods, important solute interactions were investigated with the rigorous Full Potential Linearized Augmented Plane Wave (FLAPW) method. To achieve the accuracy

demanded by this research, the FLAPW code was enhanced during the course of this program to include atomic force calculations for structural relaxation, parallelization for efficiency, and implementation of a reliable Generalized Gradient Approximation (GGA) shown to be especially important for Fe-based systems. Sequences of calculations were devised to separate out chemical, mechanical, and magnetic contributions to the boundary cohesion energetics. Origins of the chemical contributions were analyzed in terms of charge redistribution and electronic structure, the latter aided by cluster calculations. For efficiency, most calculations centered on the high-symmetry $\Sigma 3(111)$ boundary in BCC Fe, whose embrittlement behavior was confirmed in critical bicrystal experiments. With improved computational efficiency, later calculations addressed the lower symmetry $\Sigma 5(310)$ boundary to validate the generality of predicted behavior.

Initial calculations centered on the species B, C, P and S which occupy interstitial sites in the Fe boundaries, and for which quantitative effects on boundary cohesion are well established. With the implementation of full structural relaxation within the FLAPW code, the energy predictions gave excellent agreement with experiment for the relative embrittlement potencies of P and S, and the cohesion enhancement of B and C. The mechanical relaxation energy contributions were similar for the four species, the primary differences arising from the chemical contributions. The embrittling behavior of P and S is associated with a nonhybridized electrostatic interaction with Fe involving little overlap between the P and S 3p bands and the Fe 3d band, allowing a flexible redirection of bonding within the plane of the fracture surface. In sharp contrast, the B and C 2p bands overlap strongly with the Fe 3d band and directional hybridized bonding normal to the grain boundary resists in-plane redistribution on

the fracture surface. Comparison of calculations with and without spin polarization to separate magnetic contributions shows that all four species affect Fe moments similarly, with a slightly greater net reduction for the free surface environment. Consistent with the corresponding change in magnetic free energy, this decreases the embrittlement potency of the nonhybridized P and S. In contrast, due to a magnetochemical competition between magnetism and bonding, similar changes in moment have the opposite energetic consequences for the hybridized B and C. This results overall in a magnetic "damping" in which magnetism slightly reduces the potency of both embrittlers and cohesion enhancers.

The small radius of the H atom demanded implementation of GGA for accurate calculations. The predicted embrittlement potency is consistent with experimental estimates. The underlying chemical interaction is in this case more ionic in nature, with a greater charge transfer in the free surface environment causing embrittlement. The direction of charge transfer is from Fe to H, opposite to previous proposals, including the prediction of Troiano in the 1960's.

Ternary interactions were next examined to explore the manner in which substitutional segregation of alloying elements to grain boundary core sites could modify the behavior of the interstitial segregants. Substitutional Mn was found to have a direct embrittling effect, consistent with experimental observations, and shifted the effect of B, C, P, S all in the embrittling direction through enhancement of in-plane bonding. Similarly, in both ECDF and FLAPW calculations, Mo was found to increase the embrittlement potency of P through in-plane bonding, but this was more than compensated by a direct cohesion enhancing effect of Mo which cancelled the effect of P on a per-atom basis, as also supported by experimental observations. Early ECDF calculations suggested

a beneficial effect of Pd on H, but rigorous FLAPW calculations with GGA showed both the Pd-H interaction and direct effect of Pd to be weakly embrittling. This initial survey of ternary interactions, inspired by available literature evidence, found no beneficial ternary effects, and further showed such effects to be small relative to direct binary effects. Attention then focussed on the direct binary effect of substitutional alloying elements.

Based on the rigorous FLAPW calculations of the embrittling potency of Mn and Pd, and the cohesion enhancing potency of Mo, a predictive phenomenological model was developed using "handbook" parameters and key Fe grain boundary and free surface site parameters calibrated to the FLAPW results, in order to survey the effect of all transition metals on grain boundary cohesion in Fe. Using a single FLAPW calculation for Ca embrittlement of a Ni $\Sigma5(210)$ boundary, the model was also applied to alloying effects in Ni, predicting very similar chemical trends. For Fe alloys the model identified W, Re and Ru as good candidates for boundary cohesion enhancement. This was followed by rigorous FLAPW calculations for these components, confirming their relative enhancement potencies and providing more accurate energies to incorporate in materials design.

Having identified desirable alloying elements for boundary cohesion, FLAPW calculations next explored the energy difference between crystal and boundary environments defining segregation energies which were then input into grain boundary segregation kinetic theory to control grain boundary composition. Bulk thermodynamic and diffusivity databases were then extended to incorporate the desired components using available literature data. Fracture experiments in model high hardness alloys were used to correlate macroscopic boundary fracture

strength to the ideal Griffith work of separation predicted by the fundamental quantities in support of quantitative alloy design.

Integrating these results with other strength and toughness models from SRG research, prototype UHS steels and multistep thermal treatments were designed and evaluated, incorporating grain boundary W, Re and B for enhanced intergranular fracture resistance. An ultimate tensile strength of 330 ksi was demonstrated with greater than 10% ductility and a K_{IC} toughness of 47 ksi$\sqrt{in}$. Grain boundary W segregation was verified and quantified by AEM microanalysis, providing an estimate of boundary segregation entropy to supplement the segregation energy predictions in future designs. Stress corrosion measurements at NAWC are planned. The successful design and implementation of novel steels incorporating quantum mechanical predictions represents the first in a new generation of Quantum Steels.

Patent applications have been filed for both the general use of the predicted boundary cohesion enhancers and the specific steel designs incorporating them. Using principles from this research, the Northwestern spinoff company QuesTek Innovations LLC has designed a family of stainless landing gear steels now being developed under a Phase II SBIR project from SERDP (Strategic Environmental R&D Program) to eliminate the need for toxic Cd coatings in aircraft landing gear. An ESTCP (Environmental Science & Technology Certification Program) project is being proposed to certify the steels for DoD applications.

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